Theory of Rochelle salt: beyond the Mitsui model

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A simple four-sublattice order-disorder model is developed for description of phase transitions and dielectric properties of the Rochelle salt crystal. The model is developed as a generalization of the semimicroscopic Mitsui model. The symmetry properties of lattice and spatial orientations of effective dipoles connected with the asymmetric structure units in the elementary cell are taken into account. The model allows to investigate the temperature and field behaviour of transverse (besides longitudinal) components of dielectric susceptibility. The influence of the transverse electric field $\vec{E} \parallel \vec{b}$ on the phase transition points and spontaneous polarization is studied.

Key words: Rochelle salt, transverse field effect, order-disorder model
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1 Dielectric properties of Rochelle salt

Rochelle salt (RS) is a particular object in the family of ferroelectric crystals with hydrogen bonds. Despite the fact that study of its properties has a long history, the structural aspects and mechanisms of phase transitions in this crystal are not conclusively established. RS becomes ferroelectric (with spontaneous polarization parallel to the crystallographic a-axis) in the narrow temperature range between 255 K and 297 K. Both nonpolar phases are orthorhombic ($P2_12_12_1$), while the polar phase is monoclinic ($P2_111$). An elementary cell consists of four formula units.

Numerous data of structural investigations (starting from the early results obtained by the X-ray spectroscopy [1] and neutron scattering [2]) do not give a definitive answer to the question of microscopic nature of phase transitions in RS. Dielectric relaxation in the microwave frequency region and the critical slowing down around the phase transitions point to the order-disorder type scenario [3]. Alternatively, the presence of the soft mode, which was observed by the far infrared reflectivity and Raman spectroscopy in the lower paraelectric phase [4] as well as by microwave dielectric measurements [5] is rather a manifestation of the displacive-type transition.

The soft mode in paraelectric phase is connected with structure changes (such as displacement of the O(8) oxygen along the a-axis, rotation of tightly coupled water molecules with O(9) and O(10) ions) which take place at transition to the ferroelectric phase [6]; it is confirmed by the inelastic neutron scattering data [7]. Respective static displacements

are the reason of appearance of additional dipole moments of local structure units at phase transition to the ferroelectric phase.

Such displacements can be interpreted also as changes in the population ratio of two sites in the disordered paraelectric structure (revealed in the structure investigations [8, 9]). Large values of the anisotropic temperature factors can be also connected with local disorder [10]. The existence of the double atomic positions was taken into account in the so-called split-atom model for RS [11].

The order-disorder picture of phase transitions in RS forms the basis of the semimicroscopic Mitsui model [12], where asymmetry of occupancy of double local atomic positions as well as compensation of electric dipole moments induced in paraphase were taken into account. In spite of simplicity (consideration was restricted to two sublattices and induced local dipole moments were described by means of pseudospins, $S^z = \pm 1/2$), the model explains quite successfully appearance of two Curie points and effect of deuteration [12, 13].

In [14] the model was extended due to inclusion of piezoelectric coupling to the external field. One should also mention the phenomenological Landau theory [15], adapted for systems with a double critical point, which is applicable to the RS crystal in a broad range of pressure, substitution concentration of ammonium and temperature.

The Mitsui model simplifies real structure of the crystal a priori choosing the ferroelectric axis among three two-fold axes thus making an approach essentially "one-dimensional". It is obviously insufficient for more complete description of dielectric properties of the RS crystal. We can carry out a generalization, making the model "three-dimensional" and taking into account the presence of four (rather than two) translationally nonequivalent groups of atoms in the unit cell (their positions are mutually connected by elements of the point group of the crystal in paraphase [1, 2]). Such structure units are noncentrosymmetric. Effective dipole moments $\vec{\mu}_i$ ($i = 1, \ldots, 4$) can be assigned to them as a whole; the sum of these moments is equal to zero in paraphase. Changes $\Delta\vec{\mu}_i$

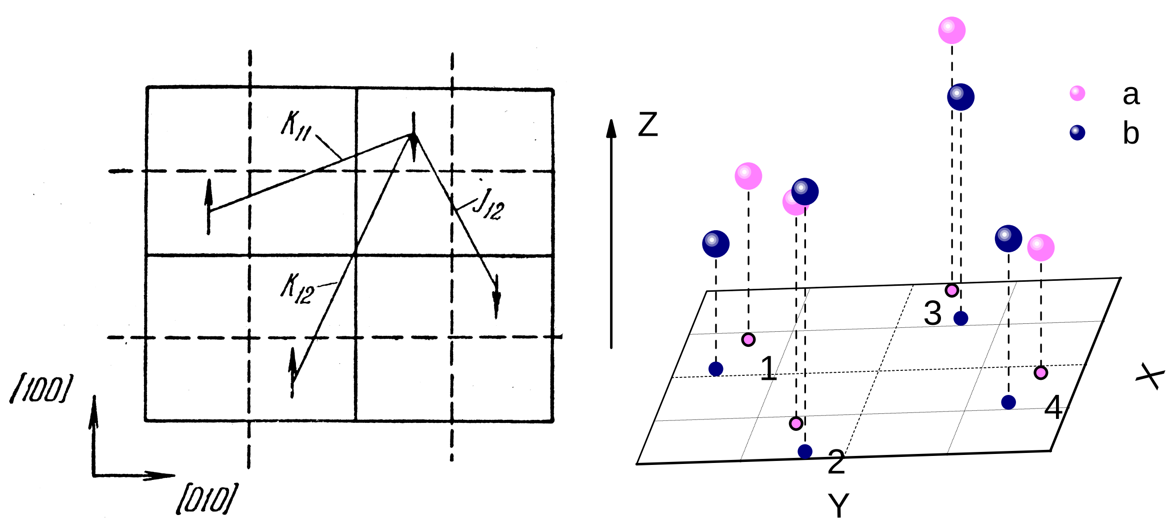

Figure 1: Orientantions of dipole moments (ordering structure units), producing resulting polarization, in the elementary cell of the RS crystal: a comparison between the classical Mitsui picture [13] (left) and the proposed approach (right). In the pseudospin formalism $\langle S^z \rangle = \frac{1}{2}(n_a - n_b)$, where $n_{a,b}$ is a probability (occupation) of respective orientation.

in such dipole moments are responsible for appearance of spontaneous polarization in the ferroelectric state. Vectors $\Delta\vec{\mu}_i$ are oriented at the certain angles to crystallographic axes and possess both longitudinal and transverse components with respect to the a-axis (Fig. 1).

Let us use the order-disorder picture for description of such changes. Taking into account double equilibrium positions of atoms we come to the effective four-sublattice pseudospin model. The model allows to calculate dielectric characteristics in any direction and to consider also the effects caused by the influence of the transverse electric field (applied perpendicularly to the ferroelectric a-axis).

In the next section we propose a Hamiltonian obeying symmetry properties of the crystal and derive expressions for main thermodynamic characteristics of RS in the mean field approximation. The obtained results of consideration of the transverse field effect on the polarization and susceptibility are presented in the third section.

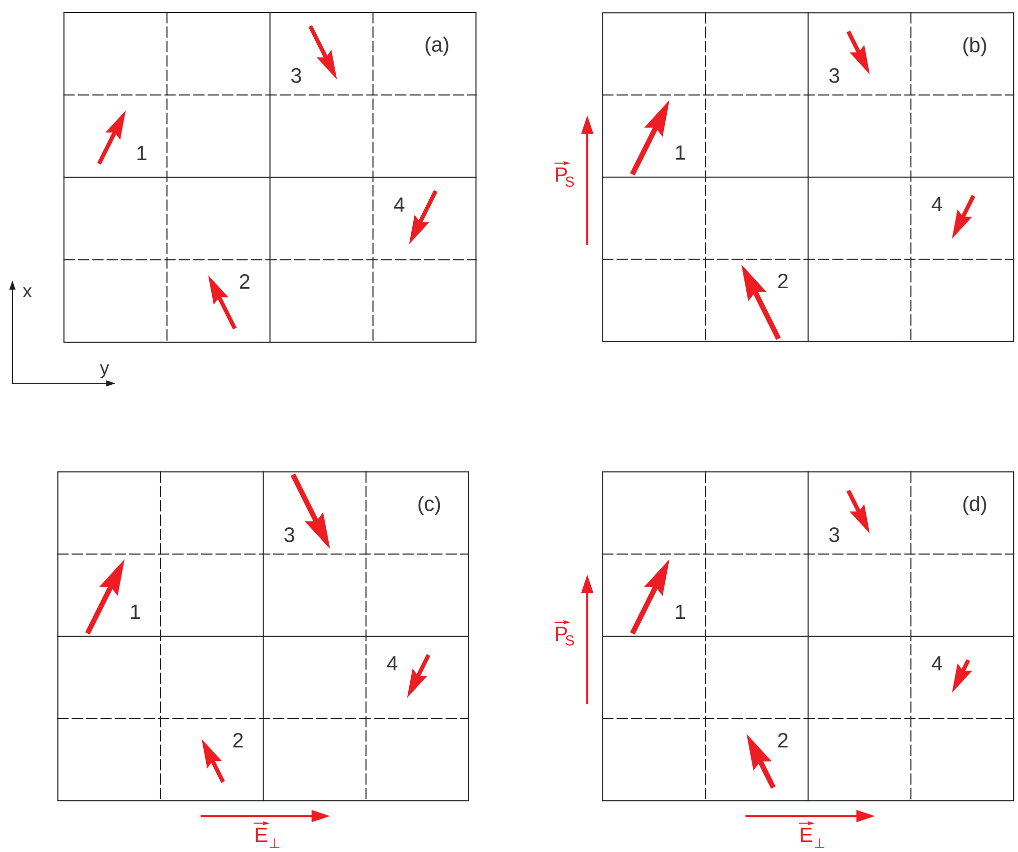

Figure 2: Orientations of vectors $\Delta\vec{\mu}_{ik}$ ($k = 1, \ldots, 4$) in a unit cell of the RS crystal and some possible dipole orderings (projection on the plane XY): (a) high symmetry phase (paraphase) – absolute values of pseudospins are equal in all sublattices; (b) ferroelectric phase with $\vec{P}_\mathrm{S} \parallel X$ – pseudospin values in sublattices 1 and 2 are larger; (c) effect of the transverse field – pseudospin values in sublattices 1 and 3 are larger; (d) $\vec{P}_\mathrm{S} \parallel X$ in the transverse field – all values are different, sublattices 1 and 2 still prevail.

2 Four-sublattice model: Hamiltonian and thermodynamics

According to the above given arguments we take the four-sublattice model as a base for simplified description of phase transitions and dielectric properties of the RS crystal. Pseudospin variables $S^z_{i1}, \ldots, S^z_{i4}$ describe the before-mentioned changes due to reordering of dipole moments of structure units: $\Delta\vec{\mu}_{ik} \equiv \vec{d}_k S^z_{ik}$. Mean values $\langle S^z \rangle = \frac{1}{2}(n_a - n_b)$ are related to differences in position occupancies in the two-minima representation of vectors $\Delta\vec{\mu}_{ik}$ (Fig. 2).

We write down the Hamiltonian of the model in the pseudospin representation:

$$
\begin{aligned}
H \;=\; & -\frac{1}{2}\sum_{i\neq j}\sum_{k} J_{kk}(i,j)S^z_{ik}S^z_{jk} - \frac{1}{2}\sum_{i,j}\sum_{k\neq l} K_{kl}(i,j)S^z_{ik}S^z_{jl} \\
& - \Delta\sum_{i}(S^z_{i1} + S^z_{i2} - S^z_{i3} - S^z_{i4}) - d_x E_x \sum_{ik} S^z_{ik} \\
& - d_y E_y \sum_{i}(S^z_{i1} - S^z_{i2} - S^z_{i3} + S^z_{i4}) - d_z E_z \sum_{i}(S^z_{i1} - S^z_{i2} + S^z_{i3} - S^z_{i4}), \qquad (1)
\end{aligned}
$$

where $J_{kk}(i,j)$ and $K_{kl}(i,j)$ describe the inter- and intrasublattice interactions respectively. The internal field Δ represents asymmetry in occupancies of the double positions. The last three terms in Hamiltonian (1) describe an interaction with components E_α ($\alpha = x, y, z$) of the external electric field. For the sake of simplicity we do not include in (1) a term describing tunnelling-like hoppings between equilibrium positions.

Formula (1) can be considered as a generalization of the Mitsui model Hamiltonian [12]: the first four terms are similar to their analogs in that model. Besides the parameter η_1, describing the ferroelectric ordering along the a-axis, and the parameter ξ, responsible for the out of phase ordering of the separated structure elements, there are new parameters η_2 and η_3 related to dipole ordering along the b- and c-axes, respectively:

$$
\begin{aligned}
&\eta_1 = \tfrac{1}{2}(\langle S^z_1\rangle + \langle S^z_2\rangle + \langle S^z_3\rangle + \langle S^z_4\rangle), \qquad \xi = \tfrac{1}{2}(\langle S^z_1\rangle + \langle S^z_2\rangle - \langle S^z_3\rangle - \langle S^z_4\rangle), \\
&\eta_2 = \tfrac{1}{2}(\langle S^z_1\rangle - \langle S^z_2\rangle - \langle S^z_3\rangle + \langle S^z_4\rangle), \qquad \eta_3 = \tfrac{1}{2}(\langle S^z_1\rangle - \langle S^z_2\rangle + \langle S^z_3\rangle - \langle S^z_4\rangle). \qquad (2)
\end{aligned}
$$

Considering Hamiltonian (1) in the mean field approximation we obtain the following equations for average values of pseudospins

$$
\langle S^z_k\rangle = \tfrac{1}{2}\tanh\left(\tfrac{1}{2}\beta H_k\right), \qquad k = 1, \ldots, 4. \qquad (3)
$$

Self-consisted internal fields H_k are given by the expressions

$$
\begin{aligned}
H_{1,2} &= (h_x + \tfrac{1}{2}\eta_1) + (h - \tfrac{1}{2}a_1\xi) \pm (h_y - \tfrac{1}{2}a_2\eta_2) \pm (h_z + \tfrac{1}{2}a_3\eta_3), \\
H_{3,4} &= (h_x + \tfrac{1}{2}\eta_1) - (h - \tfrac{1}{2}a_1\xi) \mp (h_y - \tfrac{1}{2}a_2\eta_2) \pm (h_z + \tfrac{1}{2}a_3\eta_3). \qquad (4)
\end{aligned}
$$

Here dimensionless quantities $h = \Delta/S$, $h_\alpha = d_\alpha E_\alpha/S$, $\Theta = k_{\rm B}T/S$, $\beta = 1/\Theta$,

$$
\begin{aligned}
&a_1 = [(K_{13} + K_{14}) - (J + K_{12})]/S, \qquad a_2 = [(K_{13} - K_{14}) - (J - K_{12})]/S, \\
&a_3 = [(K_{13} - K_{14}) + (J - K_{12})]/S, \qquad S = (K_{13} + K_{14}) + (J + K_{12}) \qquad (5)
\end{aligned}
$$

and the symmetry properties of interaction constants are used. The order parameters η_1, η_2, η_3 and the parameter ξ are determined from the set of equations (2–4). Thermodynamically stable solutions are those with the minimum values of the free energy. In

absence of the external field the solution $\eta_1 \neq 0$, $\xi \neq 0$, $\eta_2 = \eta_3 = 0$ corresponds to the ferroelectric phase in RS. In this case $\langle S_1^z \rangle = \langle S_2^z \rangle$, $\langle S_3^z \rangle = \langle S_4^z \rangle$ and the four-sublattice model can be reduced to the Mitsui model. After replacements $\frac{1}{2}\eta_1 \to \eta'$, $\frac{1}{2}\xi \to \xi'$ and $F/(2N) \to F'/N'$ in equations (2–4), one can obtain exactly the same formulae as in that case. Nonzero values $\eta_2 \neq 0$ or $\eta_3 \neq 0$ are induced in paraphase by the corresponding components of the external field. In the ferroelectric phase the parameters η_2 and η_3 are mutually connected. If one applies electric field along the b-axis ($h_y \neq 0$, $\eta_2 \neq 0$) to the RS crystal in the ferroelectric state ($\eta_1 \neq 0$), the third parameter η_3 automatically becomes nonzero.

3 Transverse field influence on polarization and susceptibility

The main advantage of our model is a possibility to describe the dielectric properties and polarization of the RS crystal both along and perpendicularly to the ferroelectric axis. There is also an opportunity to consider the effects induced by the external transverse field. Fig. 2 illustrates the possible dipole orderings in some important cases when field and polarization are parallel to the plane XY (ab).

Components of tensor of the dielectric susceptibility $\chi_{xx} = (2d_x/\varepsilon_0 v_\mathrm{c})(\partial\eta_1/\partial E_x)$ and $\chi_{yy} = (2d_y/\varepsilon_0 v_\mathrm{c})(\partial\eta_2/\partial E_y)$ (where v_c is the unit cell volume) are determined from the set of equations (2–4) by means of implicit differentiation. Defining $\chi_{\alpha\beta} = (2d_\alpha d_\beta/S\varepsilon_0 v_\mathrm{c})\tilde{\chi}_{\alpha\beta}$, we obtain e.g. for paraphase in presence of the field E_y:

$$\tilde{\chi}_{xx} = \frac{R_1(8\Theta - \frac{1}{2}a_3R_1) + \frac{1}{2}a_3R_2^2}{(8\Theta - \frac{1}{2}R_1)(8\Theta - \frac{1}{2}a_3R_1) - \frac{1}{4}a_3R_2^2}, \tag{6}$$

$$\tilde{\chi}_{yy} = \frac{R_1(8\Theta + \frac{1}{2}a_1R_1) - \frac{1}{2}a_1R_2^2}{(8\Theta + \frac{1}{2}a_1R_1)(8\Theta + \frac{1}{2}a_2R_1) - \frac{1}{4}a_1a_2R_2^2}. \tag{7}$$

Here $R_1 = 4(1 - \eta_2^2 - \xi^2)$ and $R_2 = -8\eta_2\xi$. In the case of the ferroelectric phase the parameters η_1 and η_3 appear besides η_2 and ξ in the expressions for χ_{xx} and χ_{yy}. Their temperature and field dependences are determined from equations (2–4).

As it follows from the analysis of behaviour of the free energy, the second order type of the phase transitions remains unchanged at $E_y \neq 0$. In such a case the transition temperatures can be determined from the equation

$$\left(8\Theta - \frac{1}{2}R_1\right)\left(8\Theta - \frac{1}{2}a_3R_1\right) - \frac{1}{4}a_3R_2^2 = 0, \tag{8}$$

which must be solved together with equations following from (3) when $\eta_1 \to 0$, $\eta_3 \sim h_y\eta_1 \to 0$.

At small values of the transverse field $R_1 = 4(1 - \xi_0^2) + o[E_y^2]$, $R_2 \sim E_y^2$, where ξ_0 is a solution of the equation $\xi_0 = \tanh\left[\frac{1}{2}\beta\left(h - \frac{1}{2}a_1\xi_0\right)\right]$. The critical temperatures shift under field proportionally to E_y^2. Signs and absolute values of the shifts ΔT_c depend on magnitudes and signs of the interaction parameters a_2 and a_3 as well as on the relation between them. From pure geometric arguments the parameters K_{12} and J include interactions between nearest and next nearest neighbours, respectively. So one can expect that $K_{12} > J$; it results in the inequality $a_2 > a_3$. When we use values $a_1 = 0.284$ and

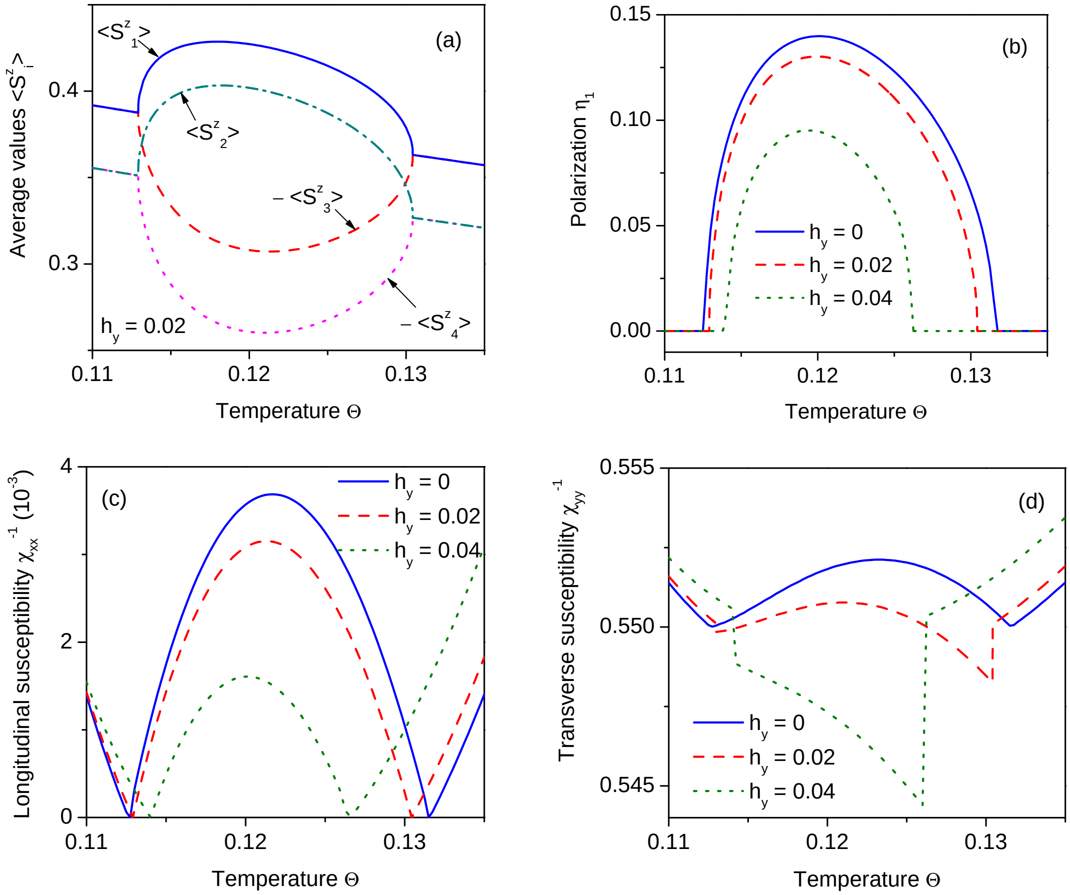

Figure 3: Temperature dependences of average pseudospin values (a), the order parameter η_1 (proportional to the spontaneous polarization) and longitudinal (c) and transverse (d) components of the dielectric susceptibility for different transverse fields at the following values of parameters: $a_1 = 0.284$, $a_2 = 0.1$, $a_3 = -0.25$, $h = 0.32$.

$h = 0.32$ chosen to obtain the best fit for critical temperatures of the RS crystal at zero field (in this case $S = 2280$ K), the numerical analysis shows that at $a_3 \lesssim -0.25$ the ferroelectric region narrows under the field E_y. The direct experimental verification is absent, but as some evidence of such a possibility we can consider the results obtained in [16, 17] by investigations of relaxation phenomena in RS under the external transverse field.

For illustration we give below numerical results for the parameter values $a_2 = 0.1$ and $a_3 = -0.25$. Temperature dependences of average pseudospin values in the cases depicted in Fig. 2(c,d) are presented in Fig. 3(a). Pairs $\langle S_1^z \rangle$, $\langle S_3^z \rangle$ and $\langle S_2^z \rangle$, $\langle S_4^z \rangle$ demonstrate a typical "Mitsui-like" behaviour but the transverse field splits their values creating difference between pairs of sublattices even in paraphase. Temperature dependences of the order parameter η_1, describing spontaneous polarization in the RS crystal, are shown in Fig. 3(b) for different values of the transverse field. One can see that such a field not only narrows the temperature range of the ferroelectric phase but can also suppress spontaneous polarization.

Temperature behaviour of components of the dielectric susceptibility is shown in Fig. 3(c,d). The inverse susceptibility χ_{xx}^{-1} goes to zero in the phase transition points both at $E_y = 0$ and $E_y \neq 0$ (Fig. 3(c)). This fact confirms that the phase transitions are

of the second order. The transverse component χ_{yy}^{-1} has jumps in the transition points at $E_y \neq 0$. Their values are proportional to the second power of the field magnitude (Fig. 3(d)). These jumps closely resemble behaviour of the transverse susceptibility of the glycinium phosphite crystals in the transverse field [18].

Let us make some numerical estimates taking into account the obtained results and using the experimental data for ε_a and ε_b components and for P_S at $E_y = 0$. The dipole moment component d_x can be determined using the maximal value of P_S in the ferroelectric phase ($P_\mathrm{S}|_\mathrm{max} = 0.25 \times 10^{-2}$ C/m^2 [19]). From the relation $P_\mathrm{S} = (2d_x/v_\mathrm{c})\eta_1$, at $\eta_1|_\mathrm{max} = 0.14$ and $v_\mathrm{c} = 1.04 \times 10^{-21}$ cm^{-3}, we obtain $d_x = 9.26 \times 10^{-30}$ C m. Respectively, for susceptibility along the a-axis we have $\chi_{xx} = 0.60\tilde{\chi}_{xx}$, and at $\tilde{\chi}_{xx}^{-1}|_\mathrm{max} = 3.7 \times 10^{-3}$ it results in $\chi_{xx}|_\mathrm{min} \simeq 160$ (such a value lies inside the experimentally observed range of χ_{xx} for ferroelectric phase, see review in [19, 20]).

Estimate for d_y component can be obtained using the relation $\varepsilon_{yy} = 1+(2d_y^2/S\varepsilon_0 v_\mathrm{c})\tilde{\chi}_{yy}$. In the ferroelectric phase region $\varepsilon_{yy} \equiv \varepsilon_b \approx 10$ (see [20]; the old experimental data show the smooth temperature dependence of ε_b in this region). At $\tilde{\chi}_{yy}^{-1} = 0.552$ we have $d_y = 17.3 \times 10^{-30}$ C m. So the Y-component of a dipole moment, connected with reordering, is nearly twice as large as the one along the ferroelectric X-axis.

Let us notice that in this case the field $E_y = 18$ MV/m corresponds to the value $h_y = 0.01$; the shift of T_c1 is $\Delta T_\mathrm{c1} \approx 0.06$ K at that field. It means that at the fields $E_y \approx 1$ MV/m the effect will be practically undetectable. The relative change of the susceptibility χ_{yy} with temperature in the ferroelectric phase region is also small ($\approx 0.5\%$). However, the results of numerical estimates can change at another choice of the parameter values a_2 and a_3, so the field effect can be much stronger. As a certain argument which points to such a possibility, we can consider the fact, that in the GPI crystal (where the effect is caused, as in RS, by the zig-zag geometry of the local dipole moment arrangement) the change of T_c is $\Delta T_\mathrm{c} \approx 0.05$ K at the transverse field $E_c \approx 1$ MV/m. It is obvious that one can check the possibility of such a noticeable effect in RS only by direct experimental investigations.

4 Conclusions

For description of phase transitions and dielectric properties of the Rochelle salt crystal we propose the four-sublattice pseudospin model developed as a generalization of the well-known Mitsui model. The introduced model takes into account spatial orientations of effective dipoles, which are related to the atomic groups in the unit cell and are responsible for the spontaneous polarization.

The model allows to investigate the temperature behaviour of both longitudinal and transverse components of dielectric susceptibility as well as to consider the influence of the transverse electric field $\vec{E} \parallel \vec{b}$. At the certain relations between the model parameter values the increase of this field can lead to the approaching of the lower and higher Curie points one to another. Our theory predicts suppression of the spontaneous polarization P_S under the field E_y. The effect is similar to the one observed in [16, 17]. The changes in the transverse susceptibility χ_{yy} in the transition points are similar to the phenomena detected in the GPI crystal [18]. As it follows from our consideration, there should exist jumps in χ_{yy} which increase proportionally to E_y^2. However, performed here numerical estimates indicate that these effects could have small magnitudes. Only future experimental studies can give a final answer.

The ideas forming the basis of the four-sublattice model can be used for description of the mixed system RS_{1-x}–ARS_x, where the significant changes in temperature behaviour of the longitudinal and transverse dielectric susceptibilities are observed at increase of the concentration x of ammonia groups and in the high concentration region ($0.89 < x < 1$) a polar phase appears with polarization along the b-axis [21, 22].

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